Pre-treatment of Rice husk with acid and base for its effect on Pyrolysis Products

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by

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CERTIFICATE

This is to certify that the thesis entitled **"Pre-treatment of Rice husk with acid and base for its effect on Pyrolysis Products",** submitted by Silla Srikanth to National Institute of Technology Rourkela, in fulfilment of the requirements of the degree of Master of Technology in Chemical Engineering is a bonafide record of the research work carried out by him, in the Department of Chemical Engineering, National Institute of Technology, Rourkela under my supervision and guidance. Mr. Srikanth has worked on this topic from August 2013 to April 2014 and the thesis, in my opinion, is worthy of consideration for the award of the degree of "Master of Technology" in accordance with the regulations of this Institute. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Silla Srikanth

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List of Abbreviations

RH	Rice Husk
RHA	Rice Husk Ash
FTIR	Fourier Transform Infrared Spectrometer
GC-MS	Gas Chromatograph and Mass Spectrometer
EDX	Energy dispersive X-ray spectroscopy
TGA	Thermo gravimetric Analysis
BSS	British Standard Sieves
ASTM	American Society for Testing and Material
HHV	Higher Heating Value
PID	Proportional Integral Derivative Controller

Abstract:

The Pre-treatment of water washing, acid washing and alkali treatment on the biomass pyrolysis was experimentally done in a stainless steel reactor. The present work is to optimize the change in the quantity and quality of the oil fraction obtained from the pyrolysis, upon the different types of pre-treatment for acid washing and alkali solutions of agricultural biomass (rice husk). Different types of pre-treatment processes were used in this work, these are water leaching, acid treatment with dilute HCl and H_2SO_4, and alkali treatments are base treatment with NaOH and KOH. The EDX analysis results were showed that the metal ions of rice husk removed by treatment with acids and bases. The influence was more remarkable using acid compared to alkali solutions. Pyrolysis was done at optimal temperature 500^oC and 5M HCl has been given the highest liquid product distribution, because it has least percentage of ions compared to all leaching processes upon the pre-treatments. The change in char percentage, and calorific values were observed. Ash content of untreated and treated biomass decreased through pre-treatment. Chemical compositions in rice husk such as extractives, hemicellulose, cellulose and lignin were investigated after pre-treatment processes. Thermal stability and decomposition rate of rice husk against acid and alkali treatments were examined by using TGA. Volatiles and moisture content of rice husk was also found using proximate analysis. The functional groups have been presented in the Pyrolysis oil, these are obtained at optimum conditions were analyzed by Fourier Transform-Infrared spectroscopy (FTIR).

Key Words: Biomass, leaching process, acid and alkali treatments, pyrolysis.

CHAPTER – 1

INTRODUCTION

1. Inroduction

Depletion of fossil fuel now days it will be going to increase next coming years. So for overcoming these solution we require to change. Therefore from the current research it has been analysed that Biomass is the one of suitable renewable resource to solve this problem. Today's although Biomass energy is a 3rd largest global source of energy in world wide. Biomass resources such as agricultural residues, sewage, industrial residues, animal residues and forestry crops [1]. Individual solid particles are characterized by their size, shape, and density. Commercial products must often meet stringent specifications regarding the size and sometimes the shape of the particles they contain. Reducing the particle size also increases the reactivity of solid; it permits separation of unwanted ingredients by mechanical products; it reduces the bulk of fibrous materials for easier handling and for waste disposal [2].

Rice husks are the hard protecting coverings of grains of rice and most widely agricultural wastes in different rice producing countries in world. It is available easily and cost of price is very low. Rice husk in rice producing countries is an extra benefit towards the use of this material. In world, about 661 million tons of rice is produced a year, after milling of this rice paddy 132 million tons of rice husk were produced. 1.3 million tons of rice is produced a year in India. Burning rice husk produced rice husk ash, if burning process is incomplete carbonized rice husk is produced. It has a high calorific vale and can be used as a renewable fuel for power generation and sometimes used for animal feed stuff, litter material as pet animals. It is difficult to ignite and it does not burn easily with open flame unless air is blown through the husk. It is highly resistant to moisture penetration and fungal decomposition. Husk therefore makes a good insulation material. It has a more silica content and which means decomposes very slowly, it also makes it a poor fodder. We cannot handle it properly because it is dusty and bulky. It has some ash content burned is 17-26%, a lot higher than fuels like wood 0.2-2%, coal 12.2% ,it means when used for energy generation large amounts of ash need to handle. It is not an easy fuel, once concern in rice husk firing is the behavior of the ash, i.e., its slagging and fouling tendency caused by a low melting point of the rice husk ash. 75-90% organic matter has in rice husk such as cellulose, hemicellulose, lignin etc. and rest minerals like alkalis, trace elements and silica. The silica in the ash undergoes structural transformations depending on the conditions of combustion such as time and temperature. Some elements play an important role in Rice husk ash such as Si, Fe, Na, Mg, Al and Ca etc. [3].Various factors which influence ash properties are incinerating

conditions (temperature and duration), rate of heating, burning technique, crop variety and fertilizer used.

Rice husk has some important applications, such as it is used as a fuel in power plant, formation of activated carbon, as a silica and silicon compounds [4], porous SiO_2 / C composite from rice husk [5], insulating fire brick using husk and other uses, like it is used as a raw material for production of furfural, acetic acid and lingo sulphonic acids. Cleaning agent in metal and machine industry, in manufacturing of building materials etc. This rice husk has been using as an industrial raw material e.g., as an building materials, activated carbon, insulating board material, , filling material, for making panel board, fillers in plastics etc. [6].

Pyrolysis is a thermochemical conversion process of biomass. Pyrolysis method is generally defined as the thermal decomposition of organic components in biomass waste in the absence of oxygen at temperature, to yield tar (pyrolysis liquid), char (charcoal) and gaseous fractions (fuel gases) [7]. Biomass basically consists of hemicellulose, cellulose, lignin, and very less ash content. Although the amount of ash is so low in biomass feed stocks, the salts, sugars and metal ions play an important role in biomass pyrolysis. Ash content is changed according to different Biomass. The amount of ash content is less in wood compared to agriculture residues. Different ways to reduce the ash content in biomass, including water washing, acid washing and alkali treatment. Water washing is given little effect on biomass, but the rate of ash content removal is less. Acid washing gives more effective to remove a largest part of ash, but it changes with different acid concentrations and depending on the structure of biomass. The effect of inorganic constituents on the thermal behaviour of biomass has been investigated. However, little work has been done on the influence of acid and alkali treatment on the pyrolysis behaviour of biomass. In this work, the ash of biomass was removed by water, acid and base washing. Pyrolysis was done at different acids and bases of pre-treatment processes. The influence of metal salts on biomass pyrolysis was obtained [8].

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestics and industrial purposes. Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas, etc. are some of the fuels. Different end uses of biomass pyrolysis products are showed in the figure [36, 38].

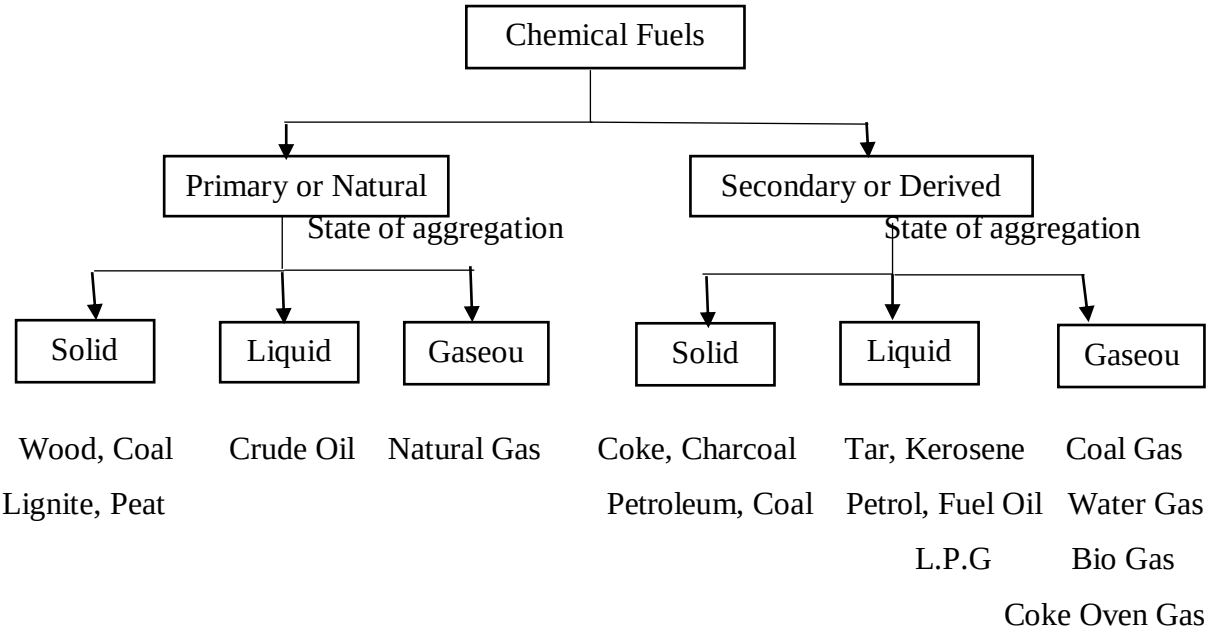

Figure 1.1 Classification of Fuels

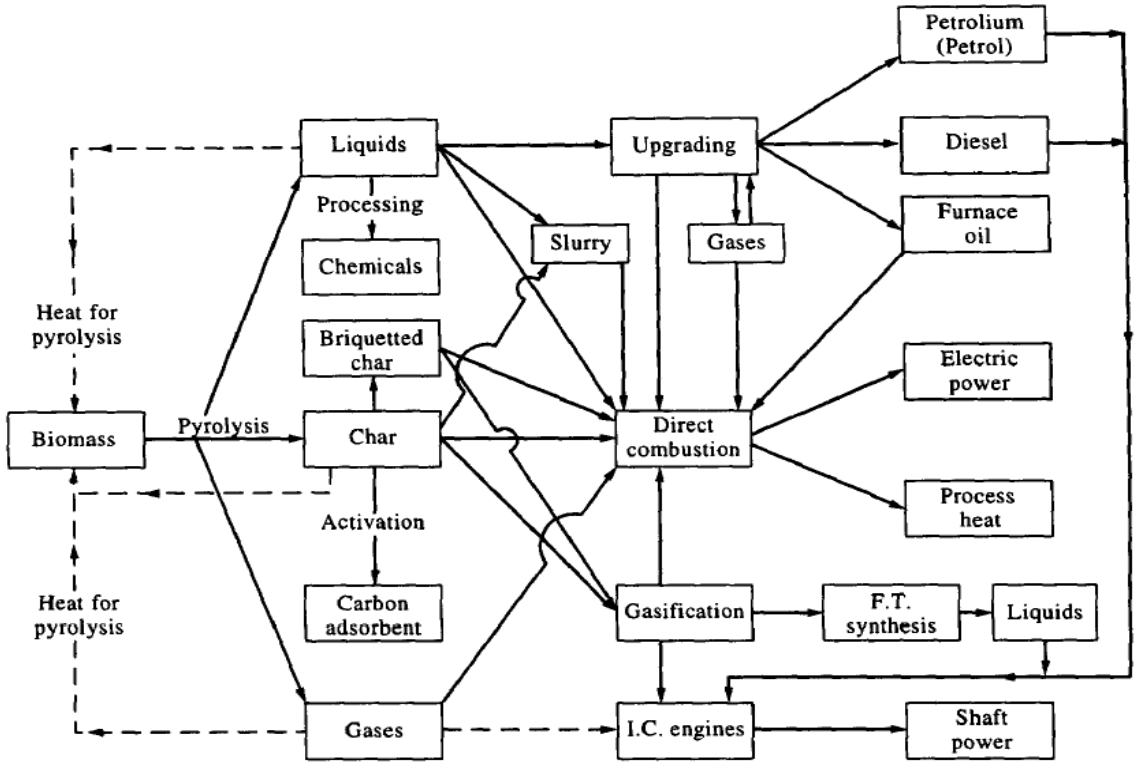

Figure 1.2 Different of uses of biomass pyrolysis products

CHAPTER – 2

LITERATURE SURVEY

2. Literature Survey

2.1 Biomass:

It is defined as biological material that has from come from animal, vegetables and plant matter. Advantages of biomass are carbon neutrality, increase bulk and energy density of biomass, source of valuable chemicals, biomass source can be decoupled from the energy utilisation [7 and 9].

2.2 Sources of Biomass:

Generally Biomass sources are available from forestry croups, agricultural residues, municipal solid wastes and Industrial residues.

Agricultural residues: Bagasse (crushed sugarcane), straw, food grain, seed hulls, corn stalks, nutshells, manure from cattle, hogs and poultry.

Municipal solid waste: Refuse-derived fuel (RDF), waste paper, yard clippings, food waste and Sewage sludge.

Biological materials: Animal waste, aquatic species, biological waste.

Forest croups: Trees, wood waste, wood or bark, sawdust, timber slash, and mill scrap.

2.3 Types of Biomass:

Today's we are using different types of biomass, such as organic fertilizer biomass, fuel Biomass, chemical biomass, feed biomass and fiber biomass [9].

- ✓ Solid waste
- ✓ Biogas and Landfill gas
- ✓ Agricultural and Wood products
- ✓ Alcohol fuels.

2.3.1 Fuel Biomass:

The Biomass, used for production of energy is known as fuel biomass. There are three different forms of energy like solid, liquid and gaseous fuel, obtained from biomass. Biomass from plants and animal origin are directly burnt for cooking and other purposes. Municipal and sewage wastes, industrial wastes and agricultural wastes are converted to energy which can meet the demand for energy in rural sector. Paddy straw and rice husk can be profitably converted to fuel gas by thermal decomposition. Ethanol, which is used as a liquid fuel can be produced from carbohydrates by alcoholic fermentation. When wood and agricultural

residues are heated in the absence of air (pyrolysis), charcoal is the resultant product which can be used as a fuel more advantageously than wood.

2.3.2 Feed biomass:

Conventionally, crop residues are used as cattle-feed. However, some of them with high percentage of lignin or non-digestible constituents need certain treatments such as soaking in water, alkali/alcohol to make their use as a fuel. The oil-cakes of various crop seed like cotton, rubber, tobacco etc. can also be used as a feed after extraction of toxic materials.

2.3.3 Organic fertilizer biomass:

The biomass used as fertilizer to soil is known as fertilizer biomass. Dry fermented slurry can be used as a direct organic fertilizer for crop land.

2.3.4 Fiber biomass:

The fibrous agricultural wastes and residues are being profitably utilized for making pulp for cheap grade paper.

2.3.5 Chemical biomass:

Highly siliceous agricultural residues like rice husk and rice straw can be converted into useful chemicals like amorphous silicon, silicate products and solar grade silicon. Furfural is another chemical, can be produced from biogases, cotton seed hulls, corn-cobs, flax fibers, oat hulls etc., which is used as a solvent for some petroleum products.

2.4 Constituents of Biomass:

Lignocellulose Biomass consists of three polymeric components, these are hemicellulose, lignin and cellulose [10].

2.4.1 Cellulose:

The first organic component of the cell wall of the biomass is cellulose. It is represented by generic formula $(C_6H_{10}O_5)_n$. Cellulose is a long chain polysaccharide formed by D–glucose units, linked by β–1, 4 glycosidic bonds: its structure has crystalline parts and amorphous ones. The below figure 2.1 is showed the molecular structure of Cellulose.

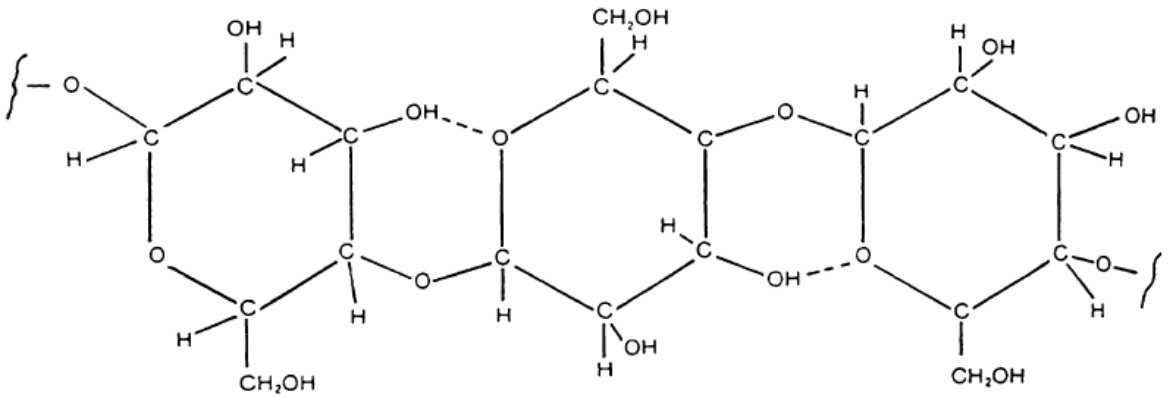

Fig 2.1 Cellulose Molecular structure

2.4.2 Hemicelluloses:

The second important constituent of the cell wall of the plant is hemicelluloses. It is represented by the generic formula $(C_5H_8O_4)$ n. The below figure 2.1 is showed the molecular structure of Hemi cellulose. It is a complex structure, branched and heterogeneous polymeric network, based on pentoses such as xylose and arabinose, hexoses such as glucose, mannose and galactose, and sugar acids. It has a lower molecular weight than cellulose and its role is to connect lignin and cellulose fibers.

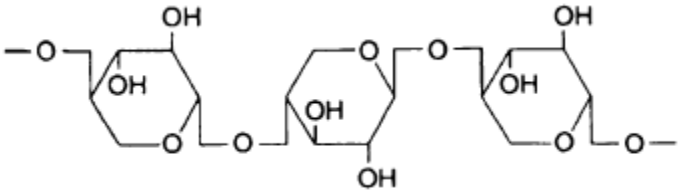

Fig 2.2 Hemicelluloses Molecular structure

2.4.3 Lignin:

The third important constituent of woody biomass is lignin, which is complex in nature, highly branch polymer of phenyl propane and is an integral part of the secondary cell walls of plants. It is primarily a three dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2.5-dimethoxyl phenol. Lignin is an amorphous polymer made by different phenolic compounds and is the main component of cell walls. Lignin holds together cellulose and hemicellulose fibers and gives support, resistance and impermeability to the planet.

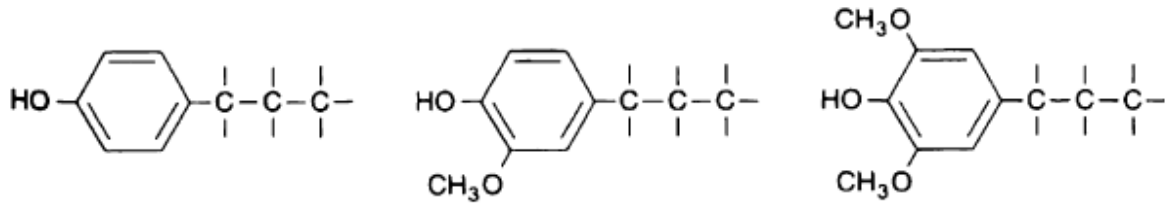

Fig. 2.3 Lignin Molecular Structure

2.5 Bio Fuel:

Bio-fuels are produced from metabolic by-products (organic or food waste products) or from living organisms. In order to be considered a bio-fuel the fuel must contain over 80 percent renewable materials. It is originally derived from the photosynthesis process and can therefore often be referred as a source of solar energy. The term bio fuel covers solid biomass, liquid fuels and gaseous fuel [11].

2.6 Different Methods of Thermal Conversion of Biomass to Biofuel

Biomass can be converted into solid, liquid and gaseous fuels by a number of processes. The technologies include thermal, thermo-chemical and bio-chemical conversions. The actual processes in these technologies are combustion, pyrolysis, gasification, alcoholic fermentation, liquefaction etc. The main products of conversion technologies are energy (thermal, steam, electricity), solid fuels (charcoal, combustibles), synthetic fuels (methanol, methane, hydrogen gas etc.) and Pyrolysis oil. These can be used for different purposes like cooking, lighting, heating, water pumping, electricity generation and as industrial and transport fuels. [12]

2.6.1 Combustion:

Combustion or burning is process of conversion of biomass into energy, where the complete oxidation of carbon taking place to CO2 and the results energy in the form of heat. It is an exothermic chemical reaction between fuel and oxidant. It includes direct burning of dried wood, cow dunk cake, burning of bagasse in boilers and results heat energy. In a complete Combustion reaction, a compound reacts with an oxidizing element, such as oxygen or fluorine, and the products are compounds of each element in the fuel with the oxidizing element.

2.4.4 Gasification:

Gasification of organics occurs at operating conditions between the complete absence of oxygen and stoichiometric (i.e., sufficient oxygen to complete the oxidation reaction).

[16].Gasification of scrap tyres seems to be an attractive method since the gaseous fuel product can be stored, transported and easily fueled for existing boilers and combustors with little modification. The characteristics of syngas evolution during pyrolysis and gasification of waste rubber have been investigated; Gasification resulted in more than 500% increase in hydrogen yield as compared to pyrolysis at 800^{o}C [17]. One of the disadvantages of the conventional gasification system is the high temperature that is require for decomposition of the feed stock and for the reforming reactions, which affect the overall energy efficiency of the process.

2.4.5 Liquefaction:

Liquefaction is the thermochemical conversion of an organic solid into petroleum-like oil. Liquefaction typically involves the production of an oil composed of heavy molecular compounds from a pyrolysis gas stream. It encourages the production of oil, which can be upgraded to transport fuels [16]. Tyres could be liquefied singly, or in combination with other waste materials and/or coal in coprocessing schemes, in one or two stage processes. The idea of including tyres into a coal liquefaction process has been proven to be more advantageous on a development plant scale. Liquefaction provides a 22 effective approach for converting the organic content into oils. Pyrolysis offers an alternative approach and is simplified since solvent is not needed.

2.6.5 Pyrolysis:

Pyrolysis is the best method to convert Biomass to bio oil, char and volatiles. It is the process of heating of organic materials the absence of air or oxygen at high temperature of 500 – 1100^{o}C. The bio oil obtained by this process contains 10-20% water [18]. Bio-oil is produced by simultaneously and rapidly depolymerizing and fragmenting the lignin, hemicelluloses and components of biomass. The compounds presents in bio-oil fall into the following five broad categories. [18] They are:

- ✓ Phenolic Compounds
- ✓ Hydroxyaldehydes
- ✓ Carboxylic acids
- ✓ Hydroxyketones
- ✓ Sugars and dehydrosugars

2.7 Factors effecting pyrolysis liquid yield:

Liquid products yield is depended on the following factors: [14]

- ✓ Design of pyrolysis
- ✓ Chemical and Physical properties of biomass
- ✓ Presence of mineral catalysts
- ✓ Gas composition
- ✓ Heating rate
- ✓ Pyrolysis temperature
- ✓ Pressure
- ✓ Residence time

2.8 Types of pyrolysis:

Pyrolysis process occurs in 3 different ways, like slow, fast and flash Pyrolysis [15].

2.8.1 Slow Pyrolysis: Slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. In slow pyrolysis, biomass was typically heated about 500^{o}C at slow heating rates (up to 10-20°C/min). The vapour residence time varies from 5 min to 30 min. Thus, the components in the vapour phase continue to react with each other, as solid char and liquid are being formed. The main product, charcoal, can be used in a wide range of areas, from domestic cooking and heating to metallurgical or chemical use as the raw material for production of chemicals, activated carbon, fireworks, absorbents, soil conditioners and pharmaceuticals.

2.8.2 Fast pyrolysis: Fast pyrolysis is a process in which very high heat flux are imposed to biomass particles, leading to very high heating rates, in the absence of oxygen. Biomass decomposes to generate vapours, aerosol and char. After cooling and condensation of the vapours and aerosol, a dark brown mobile liquid is formed which has a heating value of about half of the conventional fuel oil. Fast pyrolysis process produces 60-75 wt% of liquid bio-oil, 15-25-wt% of solid char and 10-20 wt% of non-condensable gas, depending on the feedstock used. No waste is generated because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back in the process. Fast pyrolysis uses much higher heating rates than slow pyrolysis. While slow pyrolysis is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process which is carefully controlled to give high yields of liquid.

2.8.3 Flash pyrolysis: Very fast pyrolysis is sometimes referred to as 'flash pyrolysis', usually in the context of laboratory studies involving rapid movement of substrate through a heated tube under gravity or in a gas flow. Higher temperatures and shorter residence times than fast pyrolysis are used; the main product distributions are similar to fast pyrolysis. The distinction between flash and fast pyrolysis has largely disappeared and now the term 'flash'has largely disappeared and is gradually being replaced by a more generalized definition for fast pyrolysis.

2.9 Pyrolysis Products:

The three primary products obtained from pyrolysis of biomass are char, permanent gases, and vapours that at ambient temperature condense to a dark brown viscous liquid. Maximum liquid production occurs at temperatures between 350 and 500°C [7]. This is because different reactions occur at different temperatures in pyrolysis processes. Consequently, at higher temperatures, molecules present in the liquid and residual solid are broken down to produce smaller molecules which enrich the gaseous fraction.

2.9.1 Pyrolysis liquid:

The liquid product from biomass pyrolysis is known as bio-oil. Bio-oil is not a product of thermodynamic equilibrium during pyrolysis but, it is produced with short residence times and rapid cooling or quenching from the pyrolysis temperature. This condensate is not at thermodynamic equilibrium at storage temperatures. Hence the bio-oil chemical composition tends to change toward thermodynamic equilibrium during storage [15].

Pyrolysis oil Composition:

Bio-oil obtained from Pyrolysis of Biomass contains some types of inorganic and organic compounds are mentioned below [11]:

1. Acids: Formic, acetic, propanoic, hexanoic, benzoic, etc.
2. Ketones: Acetone, 2-butanone, 2-butanone, 2-pentanone, 2-cyclopentanone, 2,3pentenedione, 2-hexanone, cyclo-hexanone, etc.
4. Aldehydes: Formaldehyde, acetaldehyde, 2-butenal, pentanal, ethanedial, etc.
5. Phenols: Phenol, methyl substituted phenols.
6. Alkenes: 2-methyl propene, dimethylcyclopentene, alpha-pinene, etc., Aromatics:
7. Benzene, toluene, xylenes, nphthalenes, phenanthrene, fluoranthrene, chrysene, etc.

The alkali metals are present in the Bio-oil, these are in the following forms:

(i). Connected to organic acids

(ii) Associated with counter ions

(iii) Related to various enzymatic compounds.

Inorganics salts and ions are present in the Bio-oil comprises of Mg, Ca, Si, Na, Fe, Ti, C, O, S and Ni etc.

Applications:

The bio-oil has some industrial applications such as,

- ✓ Combustion fuel
- ✓ Used for power generation
- ✓ Transportation fuel and could be a good substitute for fossil fuels
- ✓ Liquid smoke
- ✓ Production of chemicals and resins

2.9.2 Pyrolysis Char:

Char is a porous carbon structure that remains after the hydrogen and oxygen fractions have left the fuel. Char is often defined as the solid residue after pyrolysis. It is often polluted with other components mineral fractions and after incomplete pyrolysis, large fractions of hydrogen and oxygen that can still be present in char. Properties of char are decisively affected not only by properties of parent material but also by pyrolysis operating conditions, mainly the heating rate, the maximum temperature and the residence time at this temperature.

Pyrolysis char Composition:

Pyrolysis Char contains elements such as Hydrogen, Carbon, Oxygen and sulpur. Char also produces the various inorganic contents.

Applications of Char:

Char can be used for various industrial usages, which are discussed as follows [17],

- ✓ The char could be used for the production of activated carbon.
- ✓ It can be used further for the gasification process to obtain hydrogen rich gas by thermal cracking.
- ✓ Possibility of using this carbon feedstock for making carbon-nano-tubes may be explored.
- ✓ The char could be used as a solid fuel in boilers. The char can be converted into briquettes alone or mixed with biomass and can be used as high efficiency fuel in boilers.

2.9.3 Pyrolysis Gases:

The third main product from pyrolysis is gas. The gas mainly consists of H2, CO2, CO and CH4 together with traces of C2 species. CO2 and CO are preferentially produced at low temperature, while H2 is produced at high temperature.

Pyrolysis gases Composition:

Compositions of Pyrolysis gases such as CO, CO2 and CH4. The other components present are Butane, H2, Propylene, propane, ethane, C5 and Butanes etc.

Applications:

Pyrolysis gases basically containing very large quantity of Co_2 and along with Methane, it might have used as a fuel for industrial combustion purposes.

2.10 Pre-treatment processes:

2.10.1 Pre-treatment:

Some kind of action before the treatment, likely to be different for different raw materials and desired products [21, 22, 30].

- ✓ Some steps also before Pre-treatment
- ✓ Washing/separation of inorganic matter, pebbles, etc.
- ✓ Size reduction (grinding, milling, crushing…)
- ✓ Separation of soluble (e.g., sucrose residues)

2.10.2 Action of pre-treatment:

Pre-treatment processes are giving some kind of advantages, like modification of the structure, increased surface area, increased pore sizes, partial hydrolysis of hemicellulose.

2.10.3 Physical Pre-treatment of Biomass:

The purpose of physical Pre-treatments is the increase of the accessible surface area and the size of pores of cellulose and the decrease of its crystallinity and its polymerization degree. Several types of physical processes have been developed, such as milling, grinding, extrusion, and irradiation (gamma rays, electron beam, ultrasounds, and microwaves).These methods are not very often satisfactory if used individually, and many times are employed in combination with chemical ones in order to improve the process efficiency. The power requirement of these mechanical pre-treatments is relatively high and depends on the type of biomass and on the final particle size beyond a certain particle size, these retreatments become economically unfeasible.

2.10.4 Alkaline pre-treatments:

This treatment employes alkaline solutions, such as sodium hydroxide, calcium hydroxide or ammonia for the treatment of biomass, in order to remove lignin and part of hemicellulose and to efficiently increase the accessibility of cellulose: it is basically a delignification process, where a significant amount of hemicellulose is also solubilized. Alkaline pre-treatment has some advantages, the employment of lower temperatures and pressures than other pre-treatment technologies, in comparison with acid processes, alkaline ones cause less sugar degradation, and many of the caustic salts can be recovered and/or regenerated. Disadvantages of alkaline pre-treatment are if performed at room temperature, long times and high concentrations of base are required, alkaline reagents can also remove acetyl and various acid substitutions on hemicellulose, thus reducing the accessibility of hemicellulose.

Table 2.1: Classification of Pre-treatment Methods

Physical methods	Chemical and Physiochemical	Biological
Milling: - Ball milling - Hammer milling - Sieving **Others:** - Hydrothermal - High pressure steaming - Extrusion - Pyrolysis	**Acid:** Sulfuric, Hydrochloric and Phosphoric acids **Alkali:** NaOH, KOH and NH_3 **Gas:** ClO_2, NO_2 and SO_2 **Oxidizing agents:** -Hydrogen peroxide -Wet Oxidation **Solvent extraction of lignin:** -Ethanol Water extraction -Benzene Water extraction	**Fungi and actinomycetes** Lignin peroxidase, manganese peroxidase, lactase.

Pine wood samples were used as model feedstock to study the properties of catalytic fast pyrolysis oils. The influence of two commercial zeolite catalysts and pre-treatment of the pine wood with sodium hydroxide on pyrolysis products were investigated. The pyrolysis oils were first fractionated using column chromatography and characterized using GC - MS. Long chain aliphatic hydrocarbons, levoglucosan, aldehydes and ketones, guaiacols/syringols, and benzenediols were themajor compounds identified in the pyrolysis oils. The catalytic pyrolysis increased the polycyclic hydrocarbons fraction. Significant decreases in phthalate derivatives using SudChem and long chain aliphatics using BASF catalyst were observed. Significant amounts of aromatic heterocyclic hydrocarbons and benzene derivatives were formed, respectively, using BASF and SudChem catalysts. Guaiacyl/syringyl and benzenediols derivatives were partly suppressed by the zeolite catalysts, while the sodium hydroxide treatment enriched phenolic derivatives Pereira et.al, [22]. Zeolite catalyst and sodium hydroxide were employed together; they showed different results for each catalyst.

Ndazi et.al, [23] discussed that, thermal and chemical analysis of rice husks treated with alkali concentration of 2 to 8% w/v NaOH. Using TG and proximate analysis rice husk of thermal stability and organic compounds was examined respectively. The results indicates the proportion of lignin and hemicellulose in rice husks treated with NaOH ranging from 4 to 8% decreased significantly by 96% and 74%. Thermal stability and degradation temperatures of the alkali treated RH were lowered by 24-26%, due to degradation of hemicellulose and lignin during alkali treatment. Degradation zones in treated with alkali rice husks was a further indication that hemicellulose and other volatile substances degraded during alkali treatment. This leads to a conclusion that alkali treatment of RH with more than 4% NaOH was given a less chemical degradation and thermal stability.

The influence of acid-washing pre-treatment on biomass pyrolysis was experimentally studied in a radiation reactor. The results show that the metal ions content of rice husk treated by acids is reduced markedly. The yield of tar from pyrolysis of rice husk treated by 7% HCl increased from 41.74 to 52.88%, and the yields of gas and char decrease Hong et.al, [8].

The present work is done in the vacuum pyrolysis of deashing sugarcane bagasse, on the pyrolysis products. The objective to optimize the change in the quantity and quality of the oil fraction obtained from pyrolysis, upon pre-treatment for deashing of original bagasse. Ash, in the entrained char is believed to be catalyzing the polymerization reaction in the oils and thereby increases the viscosity. Three different pre-treatment processes were used, such as water leaching, acid treatment with HCl and HF respectively. The study indicates the

remarkable influence of pretreatment process for deashing, by enhancing the total energy distribution in oil fraction of the pyrolysis products Piyali et.al, [28].

Davidsson et.al, [29] have been taken different biomass wheat straw and wood waste. These raw materials were washed with water, acids and alkali solutions. Using these materials pyrolysis runs were done at constant heating rate in a nitrogen atmosphere. The release rate of alkali compounds from the sample is measured continuously by a surface ionization technique. Untreated biomass is releasing alkali in two interval sections, pyrolysis process connection taking place at 200-500^{o}C and pyrolysis temperature at 600^{o}C from remaining materials was come. Using vacuum pyrolysis experiments showed higher potassium alkalis and less content of sodium alkalis release. Acid washing is more effect on water washing with biomass. In the temperature at 200-500^{o}C water washing reduces the alkalis from wood waste and wheat straw by 5-30%, through acid washing is more effect and reduces the emission by around 70%. Experiments with pure cellulose ash content 0.07% indicate that the washing methods are in effectives in removing alkali bound to the organic structure of the biomass.

CHAPTER – 3

EXPERIMENTAL SECTION

3. Experimental Section

3.1 Raw material:

Rice husk is chosen for the present work, this material was purchased from rice mills. The rice husks were sun dried for few days to remove the moisture content, after which they were ground in a high speed rotary grinding mill and screened by using British standard sieves (B.S.S. Mesh no 60). After sieving, separator to give fraction like 0.25mm or 250µm, this is the particle size of rice husk were taken for the experiment. After which we have been kept in oven at 50^0C in 24 hour for removing moisture. These samples have to be put in zip lock packs and kept in dusk.

3.2 Pretreatment Processes:

Pre-treatment is an any treatment received before some other process. Rice husks have been taken to different types of treatments in this work. The pre-treatment processes selection is based on the literatures [8, 27, 28, and 29]. Main aim of this pre-treatment processes is extract the maximum ash content. The treatments such as water leaching, leaching with different molars of HCl, H_2SO_4, NaOH and KOH, these are the deashing and debasing treatments respectively. The details of leaching treatments are shown in the following table 3.1.

Table 3.1 Different types of Pre-treatment Processes

Treatment No.	Leaching Process	Soaking/Leaching Time
1	Water Leachig (Milli Pore Water)	1hr
2	Water Leachig (Milli Pore Water)	24hr
3	Leaching with 2.5M HCl Solution	1hr
4	Leaching with 5M HCl Solution	1hr
5	Leaching with 0.2M H_2SO_4 Solution	1hr
6	Leaching with 0.6M H_2SO_4 Solution	1hr
7	Leaching with 1M H_2SO_4 Solution	1hr
8	Leaching with 1M NaOH Solution	1hr
9	Leaching with 5M NaOH Solution	1hr
10	Leaching with 1M KOH Solution	1hr
11	Leaching with 3M KOH Solution	1hr

*****240 ml leachate corresponds to 20gms of Rice husk*****

Above pre-treatment processes were done at room temperature only. For all these treatments mixtures have been leached and stirred occasionally for respective socking times at room temperatures. After which the samples were filtered off and collected the leachates, kept in refrigerator for finding sugar content. The residue was filtered with distilled water. This process was continued till water remained neutral, which means have to be removed ions and salts. After this residue was collected and kept in oven at 105^{o}C for removing the moisture.

3.3 Thermal analysis of raw material using TGA:

The thermo gravimetric analysis (TGA) of raw materials were done using the DTG 60 instrument. The apparatus is used a horizontal differential system balance mechanism. The sample capacity of each rice husk material is like 6-8 mg. Samples were placed in a platinum container. TG analysis of all pre-treated samples were done at heating rate of 10^{o}C/min. These samples were heated at room temperature to 700^{o}C. The thermo gravimetric weight loss curve (TG, Wt. %) were verified as a function of temperature. The TGA analysis of the samples such as water acid and alkali treatments were analysed and weight loss was calculated from the TG curve. TG analysis of different samples depends on the amount of cellulose, hemicelluloses and lignin content [31].

3.4 Different Analysis of treated and normal Rice husk:

Treated and untreated Rice husk materials were characterized according to their proximate analysis, CHNS, calorific values, EDX analysis and compositional analysis. [32].

3.4.1 Proximate analysis

Proximate analysis is used to give the percentage of moisture, volatile matter, ash and fixed carbon content (by difference) in the respective materials. For ASTM standard of D-3172((proximate), D-3173 (moisture), D-3174 (ash content), D-3175 (volatile matter).

(a). Moisture content:

About one gm of finely powered air-dried sample is weighed in a crucible is placed inside an electric a hot air-oven, maintained at 105^{o}C-110^{o}C. The crucible is allowed to remain in oven for one hour and then taken out, cooled in a desiccator and weighed. Loss in weighed is reported as moisture.

Percentage of moisture = Loss in weight*100 / Wt. of sample taken

(b). Volatile matter:

The dried sample of rice husk left in the crucible in (1) is then covered with lid and placed in an electric furnace like muffle furnace, maintained at 925±20^{o}C. The crucible is taken out of

the oven after 7minutes of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage basis.

Percentage of Volatile matter

= Loss in weight due to removal of volatile matter * 100 / Wt. of sample taken

(c). Ash:

The residual sample in the crucible in (2) is then heated without lid in a muffle furnace at 525±20^{o}C for one hour. The crucible is then taken out, cooled first in air, then inside a desiccator and weighed again. The residue is reported as ash on the percentage of basis.

Percentage of Ash = Wt. of ash left * 100 / Wt. of sample taken

(d). Fixed carbon:

Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash)

3.4.2 Ultimate analysis:

The ultimate analysis was carried out in CHNSO elemental analyzer (Vario El Cube Germany) to know the elemental composition.

3.4.3 Calorific value analysis:

The calorific value of a fuel is nothing but the heat of combustion of the fuel (ASTM D5865). It is defined as the total quantity of heat produced when a unit mass or volume of fuel is completely burnt with pure oxygen. It is also said to be the heating value of the fuel. In this reaction the sample and the oxygen are initially at the same temperature and the products of combustion are cooled to with in a few degrees of the initial temperature, also the water vapor formed by the combustion is condenced to the liquid state. Thus the term calorific value as measired in a bomb calorimetr denotes the heat liberated by the combustion of all carbon and hydrogen with oxygen to form carbom dioxide and water.

3.4.4 EDX Analysis:

The elemental compositions of rice husk ash was found by using EDX (Energy dispersive X-ray spectroscopy). These ash samples were put on carbon tape and coated with Zn. Oxygen is sent by this process with 2 bar temperature. EDX was done how much percentage of impurities were obtained in elements through rice husk ash.

3.4.5 Component analysis of treated and untreated biomass:

Percentage of extractives, hemicellulose, lignin and cellulose has been found through component analysis [33].

(a) Extractives Analysis:

Dried Rice husk sample (R_0, g) was leached with the mixture of Ethyl alcohol / benzene (1:2 in volume) at room temperature for three hours. Air drying, the residue was dried in a hot oven at 105–110^{o}C for constant weight. The residue was cooled in a desiccator and then weighted (R_1, g). The extractive wt. percentage is calculated as by using below formula.

$$W1\ (wt.\%) = \frac{Ro - R1}{Ro} * 100$$

(b) Hemicellulose Analysis:

The residue R_1 gms from the extractive analysis is put in a conical flask and then add it into 150 ml of NaOH solution (20 gms/lit). Then the mixture were boil for 3.5 hours with the recycled distilled water. The residue was filtered with distilled water. This process was continued till water remained neutral, which means have to be removed ions and salts, and Air drying, the residue was dried in a hot oven at 105–110^{o}C for constant weight. The residue was cooled in a desiccator and then weighted (R_2, g). The hemicellulose wt. percentage is calculated by using below formula.

$$W2\ (wt.\ \%) = \frac{R1 - R2}{Ro} * 100$$

(c) Lignin Analysis:

Put 1 gm of extractives analysis residue was weighed into a flask and, and Air drying, the residue was dried in a hot oven at 105–110^{o}C for constant weight. The sample was then cooled in a desiccator and weighed (R_3, g). Slowly pour 30 ml of H_2SO_4 with 72% concentration into the sample. This mixture was kept at 8 –15^{o}C for 24 hours. Then transfer it into a conical flask and dilute it with 300 ml of distilled water. Then the mixture was boil for 1 hour with the recycled distilled water. The residue was filtered with distilled water. This process was continued till water remained neutral, which means have to be removed ions and salts. The residue is cooled in a desiccator and then weighted (R_4, g). The lignin wt. percentage is calculated as by using below formula.

$$W3\ (wt.\%) = \frac{R4(1 - W1)}{R3} * 100$$

(d) Cellulose Analysis:

The cellulose wt. percentage is calculated as,

$$W4\ (wt.\ \%) = 100 - (Extractives + W_1 + W_2 + W_3 + W_4)$$

3.5 Experimental set up:

Fig 3.1, shows the experimental set up of the biomass pyrolysis experimental set up and Fig 3.2, the schematic diagram. The Pyrolysis unit consists of Pyrolysis reactor, electrically heated furnace, PID controller, glass condenser and measuring cylinder. The temperature of the furnace was maintained by highly sensitive PID controller.

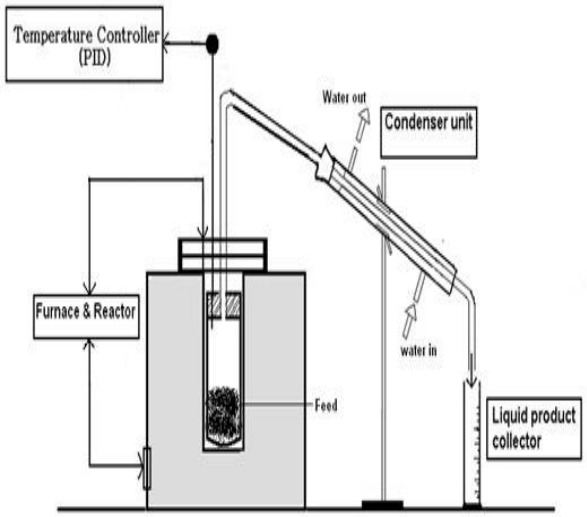

Fig 3.1, 3.2 Experimental set up and Schematic diagram experimental setup of Biomass Pyrolysis respectively

3.5.1 Reactor specification:

The reactor (Fig 3.3) is cylindrical shaped vessel made up of stainless steel (SS: 316 B grade) having capacity of ½litter. The pyrolysis experiments were performed in an apparatus designed with a batch reactor of height 16.5cm, 4.0 cm ID, OD 4.7 cm. in diameter and thickness is 0.35cm.

Fig 3.3 Reactor for using pyrolysis experiments

3.5.2 Experimental Procedure:

The rice husk materials were purchased from the market and after the dried rice husk samples to pass through 60mesh sieve (250µm) has been taken directly as feed to the reactor. These experiments were done in a semi batch reactor of pipe made up with stainless steel. This reactor was electrically heated at a optimal temperature of 500^{o}C with a heating rate of 20^{o}C/min. At the time of reaction, the vapors from the reactor was condensed in a water cooled condenser and the non-condensable gas was vented to atmosphere. The condensed oil was collected from the outlet of the condenser in a measuring cylinder, and weighted. The remaining residue collected and weighted after cooling the reactor**.** The weight of non-condensable gases was measured by mass balance. Total liquid contains aqueous and fuel, these layers were separated by using gravity separator. Same procedure was done by treated samples also.

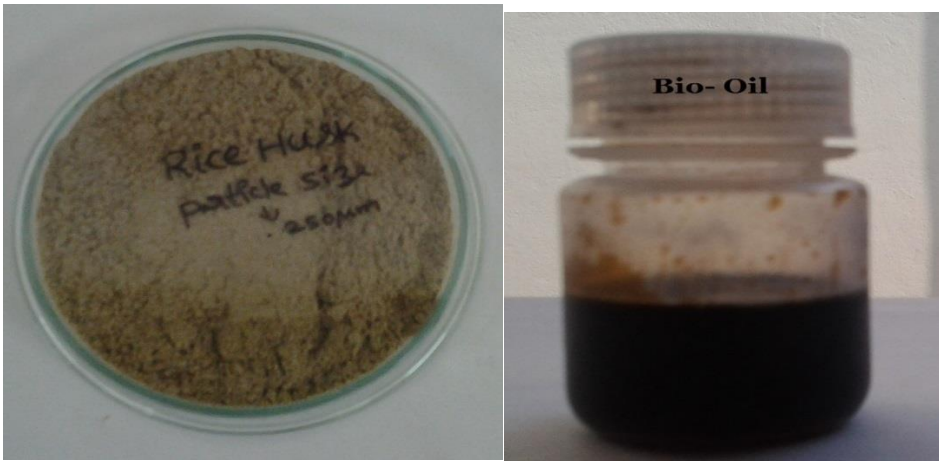

Fig 3.4 Pictures of rice husk and bio-oil from pyrolysis of rice husk

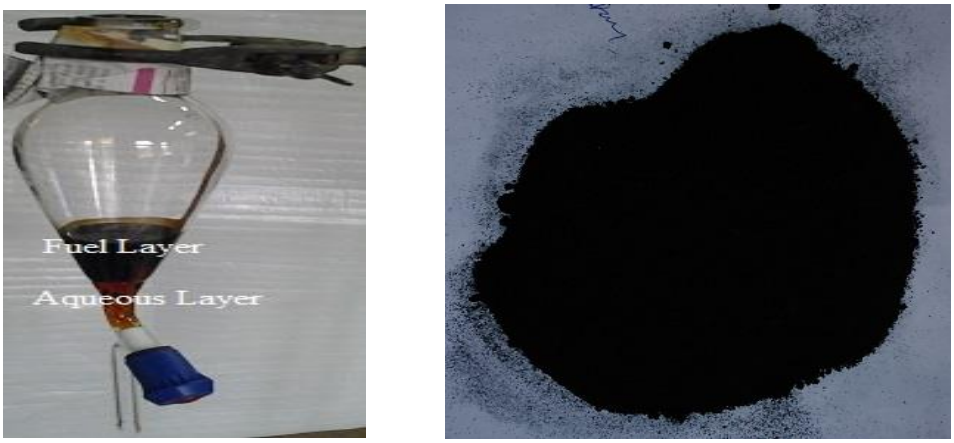

Fig 3.5 Gravity separator and rice husk Char after pyrolysis

3.6 Determination of pH and Calorific values of treated and untreated pyrolysis oil:

Pyrolysis oils were obtained through characterized for their chemical and physical properties. The physical properties like calorific value, pH etc., of all treated and untreated pyrolysis oils were found and mentioned in the results part. The pH of the samples have been determined using the pH meter EUTECH pH 510. The calorific values have been measured using bomb calorimeter.

3.7 Determination of functional group of Pyrolysis oil

Fourier Transform Infrared spectroscopy (FTIR) of all Pyrolysis oils obtained at temperature of 500^{o}C were analysed in a Perkin-Elmer infrared spectrometer with a resolution of 400 cm^{-1} and in the range of 400 - 4000cm^{-1} to know the functional group present in the pyrolysis oil.

CHAPTER – 4

RESULT AND DISCUSSION

4. Result and Discussion

4.1 Characterization of treated and untreated rice husk:

The proximate analysis is used to determine the moisture, volatile matter, Ash, fixed carbon (by difference) content in the rice husk upon the pre-treatment processes. It is a quick and practical way of assessing the fuels quality and type. The moisture of biomass has a marked effect on the conversion efficiency and heating value. Higher moisture of biomass has a more tendency to decompose resulting in energy loss during storage. Volatile matter evolves in the form of gas, light, hydrocarbon and tars. Volatile matter of the biomass is higher than the coal (around 75%). Higher volatile matter of the biomass makes it more readily devolatilized than solid fuel. Liberating less fixed carbon hence makes them more useful for pyrolysis and gasification. Ash content and moisture content affect the heating value. The ash content in the bio mass is an integral part of plant structure which consists of a wide range of mineral matter such as salt of calcium, potassium, silica and magnesium. Ash content depends upon the plant and soil condition in which the plant grows. The proximate of all raw materials are given in Table 4.1, which shows that the raw materials contains higher percentage of volatile matter and less amount of moisture and ash content.

Table 4.1 Proximate analysis of untreated and treated Rice husk

Raw material	Moisture (Wt. %)	Volatile matter (wt. %)	Ash (wt. %)	Fixed Carbon (wt. %)
Normal Rice husk	8.4	64.6	16	11
Leaching with water (24hr)	7	69	14.4	9.6
5M HCl (1hr) treated RH	6.7	68	10	15.3
1M H_2SO_4(1hr) treated RH	7	69	10	14
3M KOH(1hr) treated RH	9	68	8.9	14.1
5M NaOH(1hr) treated RH	6.3	69	9.3	15.4

4.2 Effect of different deashing and alkali solutions treatments on rice husk:

Treated with water, acids and bases has been given some effects on rice husk material, it was observed. Those are ash removal, elemental compositions, calorific values and chemical compositions.

4.2.1 Ash percentage in rice husk:

All biomass samples like untreated and treated, were kept in muffle furnace at 525±25^{o}C for finding ash content, which have small amount of unburnt carbon. The ash was found and varying upon the different types of pre-treatments. The ash percentage in both treated and normal rice husks are presented in the following table 4.2. It is shown that compared to untreated and treated rice husk samples ash content was decreased. Normal rice husk has higher ash, compared to other treatments. Water leaching rice husk has been given a moderate ash removal. Treated with H_2SO_4 was given less ash compared to water leaching ash. 5M HCl treated rice husk has been given 10 wt. % of ash. The good result was obtained from treated with 5M NaOH, it has given 8.9% of ash content [28, 34].

Table 4.2: Percentage of ash in rice husk using different treatment methods

Leaching Process	Wt % Ash
Normal Rice husk	16
Treated Sample	
Leaching with water (1hr)	15
Leaching with water (24hr)	14
0.2M H_2SO_4	13.2
0.6M H_2SO_4	11
1M NaOH	11
2.5M HCl	12.1
1M H_2SO_4	10
1M KOH	10.2
5M HCL	10
3M KOH	9.3
5M NaOH	8.9

4.2.2 Elemental composition of Rice husk:

Rice husk ash elemental composition was analyzed by using EDX (Energy dispersive X-ray spectroscopy) and shown in the below table 4.3. Rice husk ash has some elements like Na, Fe, Si, Ca, Al, Mg, K, Ti and Zn [34]. We have to be removed ions in rice husk because it is played important role. Due to water, acid and alkali washing has been removed some ions in rice husk ash. Normal rice husk ash has been given the higher percentage of impurities. However, the other compositions were found in this study are due to equipment used, geographical factors and sample preparation. Unburnt carbon also found in ash. Chemical compositions in the rice husk ash is considered as silica materials contain mainly of silica content. It is shown that rice husk ash consists in the range of 15 % to 4.49% Si. Water washing higher time as removed less content of elements. Alkali solutions such as NaOH and KOH removed Ca, Mg, and Na ions. Rice husk was treated with HCL solution, it is removed Na and Ti elements. Finally, it has been removed less amount of ions content.

Table 4.3: Elemental compotions of Untreated and Treated Rice husk

Elements	Normal Rice Husk (%)	Water Leached 24hr RH (%)	5M HCL Treated RH (%)	1M H_2SO_4 Treated RH (%)	5M NaOH Treated RH (%)	3M KOH Treated RH (%)
Si	15.49	5.79	5.69	10.45	7.63	4.79
Fe	0.55	0.13	0.13	0.30	0.27	0.06
Ca	1.58	0.26	0.54	2.36	0.93	1.7
Al	0.08	0.07	0.08	0.13	0.04	0.04
Mg	2.44	0.63	0.61	0.14	1.60	3.66
Na	0.14	0.09	ND	ND	0.13	0.1
K	0.39	0.05	0.04	0.05	0.05	0.10
Ti	0.02	0.03	ND	0.02	0.04	0.04

4.2.3Higher Heating Value of untreated and treated rice husk:

Calorific values of rice husk material was observed using bomb calorimeter. Treated and untreated rice husk calorific values were shown in below table 4.4. Calorific values are increased due to acid washing and alkali treatments. Normal rice husk samples are given 17.74 MJ/kg [23]. Washing with water at 24hrs gave the higher calorific value compered to normal rice husk that observed. 5M HCl solution is given the highest calorific value compared to all treatments, because it has been removed some salts and alkali ions.

Table 4.4: Higher heating values of treated and untreated rice husk

Biomass	HHV (MJ/kg)
Untreated(1hr) RH	17.74
Water leached(24hr) RH	18.96
5M HCl (1hr) treated RH	20.09
1M H_2SO_4(1hr) treated RH	18.13
3M KOH(1hr) treated RH	18.48
5M NaOH(1hr) treated RH	18.61

4.2.4 Chemical compositions of untreated and treated rice husk:

Optimize the change in the chemical composition of rice husk due to different pre-treatments. The chemical compositions such as extractives, hemicellulose, cellulose and lignin of all biomass untreated and treated was also found by the procedure of literature. Below table 4.5 gives the chemical compositions of both treated and untreated rice husk. Product distribution of Pyrolysis is relates the chemical composition of rice husk has given in the table. Water washing (24hr) case, the extractives were washed out and decreasing the extractives wt. % from 28.8 to 8.53 [28]. This is attributed to the fact that unlike wood biomass, extractives of rice husk comprise largely of sugars and starch are washed in water leaching (24hr). Main content of cellulose is not changed. Leaching with HCl solution has 17.67 wt. % extractives, cellulose is higher compared to hemicellulose and lignin content [40].

Table 4.5: Chemical composition of untreated and treated rice husk

Biomass	Extractives wt%	Chemical composition		
		Hemicellulose wt%	Cellulose wt%	Lignin wt%
Untreated(1hr) RH	28.8	23.87	37.15	14.18
Water leached(24hr) RH	8.53	28.2	45.24	18.03
5M HCl (1hr) treated RH	17.67	9.28	69.15	3.9
1M H_2SO_4(1hr) treated RH	13.15	21.56	49.28	16.10
3M KOH(1hr) treated RH	9.23	20.59	48.26	21.92
5M NaOH(1hr) treated RH	7.76	27.48	47.24	17.52

4.3 Thermal and decomposition Analysis of normal and leached rice husk material :

Biomass is basically consists of three major components such as hemicellulose, lignin and cellulose. Each component degradation at different rates based on their elemental composition, temperature and structure of the biomass. Hence, the same kinetic parameters cannot be used to predict the thermal behavior of the samples throughout its thermal transition. It is thus critical to identify the degradation temperature range of individual components and to apply the kinetic parameter for each component [31].

The results of the thermo gravimetric (TGA) and differential thermo gravimetric (DTA) analyses obtained at 10^{o}C/min for RH samples at different grinding time are graphically presented in Fig 4.1. Generally, the test results show that the thermo gravimetric curves decreased with increasing temperature. This is due to the carbonisation and decarbonation of rice husk. TGA of normal and pre-treated rice husks is shown in figure, both untreated and pre-treated rice husk samples started to undergo initial weight losses between 42 to 200^{o}C, this step involves the removing moisture and other primary volatile substances in the respective rice husk material. Initial degradation is started from 225^{o}C, involving decomposition of secondary compositions cellulose. 3rd stage of this thermal degradation is started from 355^{o}C to 545^{o}C main volatile components such as hemicellulose and lignin. Last stage is like ash content of all rice husk samples [42, 43, and 44].

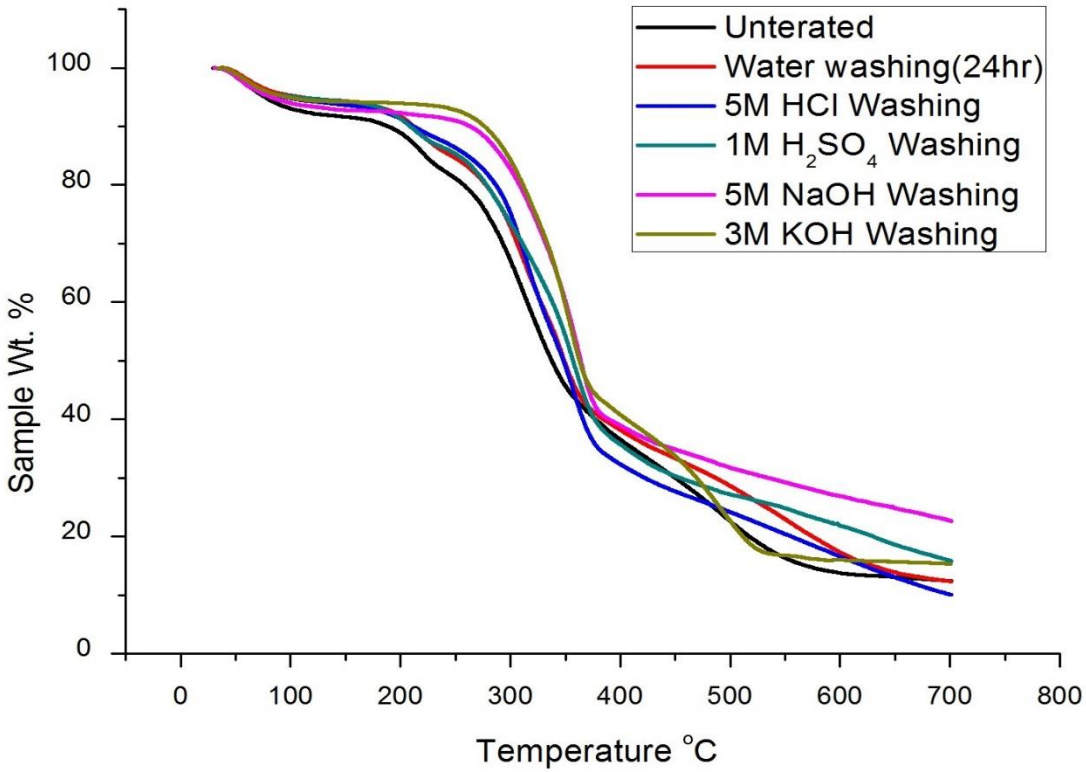

Fig 4.1 Effect of pretreatment processes on thermal stability of rice husk

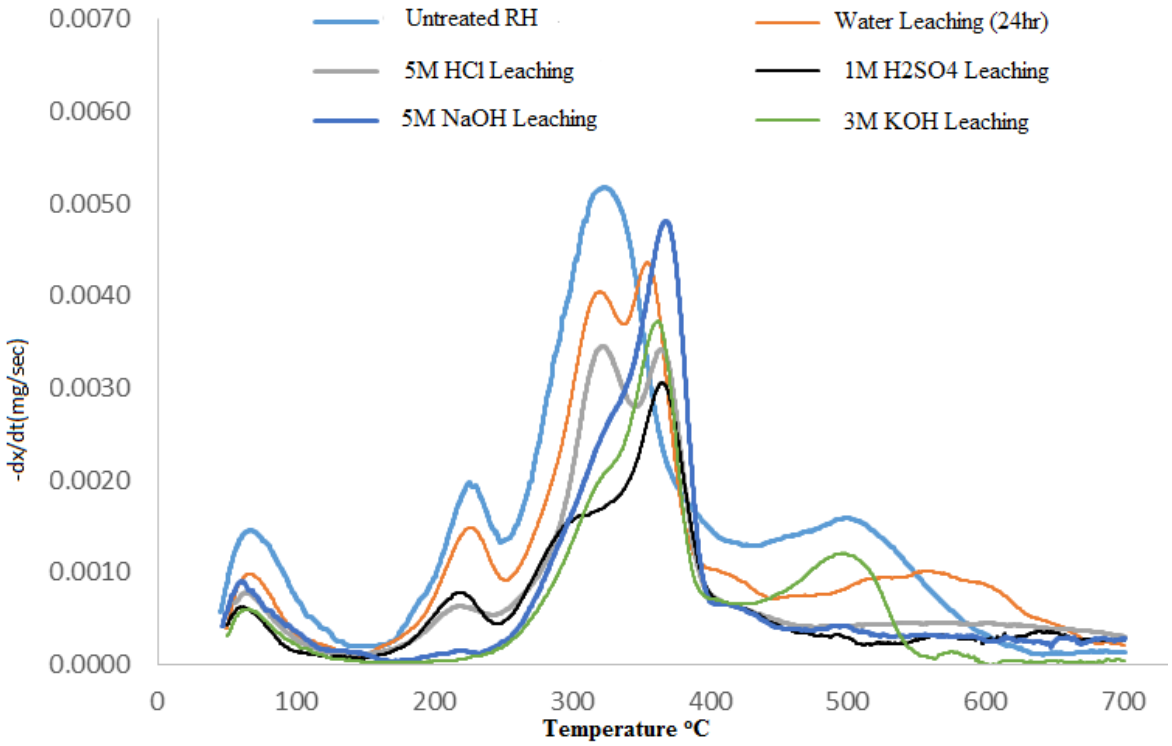

Fig 4.2 Effect of pretreatment processes on decomposition rate of rice husk

4.4 Effect of acid washing and alkali solutions treatments on pyrolysis product distribution of rice husk:

The yields of resulting products from the medium pyrolysis of rice husk of both treated and untreated were studied under the effect of pyrolysis temperature, heating rate, holding time, sweep gas (i.e., nitrogen) flow rate, condensation temperature and particle size. First, to determine the effect of pyrolysis temperature, heating rate and holding time on the pyrolysis product yields, experiments were conducted at particle size of 250µm, in combustion only and condensation temperature of 10°C and their results were shown in table and figure. Second, to examine the effect of condensation temperature on the pyrolysis product yields, experiments were carried out at the optimal pyrolysis conditions determined at 500°C. Finally, to relate the effect of particle size on the pyrolysis product yields, experiments were also performed at the optimal pyrolysis conditions determined.

All the pyrolysis runs were done at 500°C, because it is observed at 500°C has been given the optimum temperature of rice husk sample. The yield of three products (liquid, char and gas) as a function of temperature only. Below table 4.6 is showed the relation between the bio-oil of both treated and untreated samples, from this table bio-oil yield is increasing, when the sample is treated with water washing, acids and alkali solutions. Un condensable gases wt. % is decreased and finally char also decreased. Increase in the total liquid percentage in 5M HCl leaching case is 57.05% [8]. Water washing with 1hr socking time, it was a little effect than untreated. In case of leaching with least possible water 1hr and longer period 24hr the increase is by 31.3 % and 43.95 % respectively. A special reference has to be made to explain the increase in the oil percentage for treated bagasse. It was observed that upon acid washing and alkali treatments, both the amount of the rate of their evolution and volatiles increase [28]. The oil fraction consists of mainly the condensates of primary vapours from lignin and cellulose etc., increases only when the absolute values of cellulose and lignin increase and/or when the secondary cracking of oil to give lighter organic fraction occur. Thus, the increased devolatilizationrates in combination with changed organic chemical composition are responsible for the increase in oil fraction as well as oil to total liquid ratios. Similar increase in oil percentages has been reported [38, 41] for other biomass also wherein reduction of ash is considerable during pre-treatment.

Table 4.6: Untreated and Treated Rice husk Pyrolysis Product Distribution

Biomass	Total Liquid(%)	Oil (%)	Char (%)	Gas (%)
Normal Rice Husk	29.7	16.80	38.15	32.15
Water Leached Rice Husk (1hr)	31.3	17.01	37.35	31.35
Water Leached Rice Husk (24hr)	43.95	23.67	33.1	23.39
0.2M H_2SO_4 Treated RH	41.75	21.89	34.6	23.65
0.6M H_2SO_4 Treated RH	43.95	23.67	33.45	22.3
1M H_2SO_4 Treated RH	47.05	25.18	32.75	20.2
2.5M HCL Treated RH	53.25	27.92	32.45	14.3
5M HCL Treated RH	57.05	32.14	31.55	11.4
1M NaOH Treated RH	31.55	17.28	36.9	31.55
5M NaOH Treated RH	32.46	20.53	36.93	30.61
1M KOH Treated RH	31.65	18.47	36.98	31.37
3M KOH Treated RH	34.76	19.94	35.28	29.95

*****240 ml leachate corresponds to 20gms of Rice husk*****

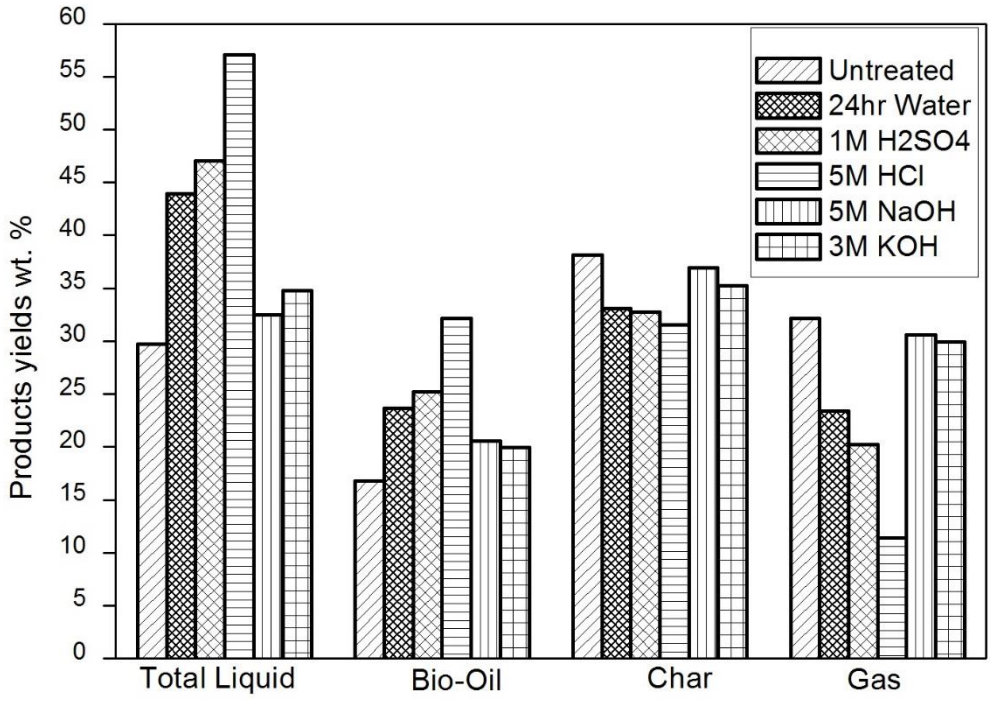

Fig 4.3 Pyrolysis products distribution of rice husk pretreated by different acids and bases

4.5 Effect of deashing and alkali solutions treatments on pyrolysis product characteristics of rice husk:

The Pyrolysis products of treated and untreated rice husk have been found to different analysis for their properties. The effect of acid washing and alkali solution treatments on the characteristics of pyrolysis product is reported in the following different sections.

4.5.1 Calorific value and pH of rice husk pyrolysis oil:

Calorific value or higher heating vale (HHV) and pH of treated and untreated rice husk oil has been shown in the below table 4.7. Here there is a variation in the calorific value of treated and untreated rice husk pyrolysis oil. A fuel should possess high calorific value, since the amount of heat liberated and temperature attained depends upon the calorific value of fuel. Higher calorific valves were observed, especially in treated pyrolysis oils. Most of the bio oil have a pH in the range of 2.0 to 4.2. Because in these oils organic acids are presents, like mostly formic acids and acetic acids. 5M HCl treated rice husk has given the highest calorific value (34.92 MJ/kg) and pH (3.2) respectively [1, 25].

Table 4.7: Properties of pyrolysis oil from Rice husk

Biomass pyrolysios oil	Higher heating value (MJ/kg)	pH
Untreated(1hr) RH	34.48	2.8
Water leached(24hr) RH	31.43	2.9
5M HCl (1hr) treated RH	34.92	3.2
1M H_2SO_4(1hr) treated RH	32.16	2.8
3M KOH(1hr) treated RH	31.82	2.7
5M NaOH(1hr) treated RH	32.63	2.8

4.5.2 FTIR analysis of untreated and treated pyrolysis oil:

Rice husk pyrolysis oil both untreated and treated biomass was analysed for their compounds using Fourier transform infrared spectroscopy (FTIR). FTIR is a technique, it is used to obtain an infrared spectrum of absorption and emission of a liquid, gas or solid. It has been given the functional groups of treated and untreated rice husk pyrolysis oil. The FTIR spectra were done in the range of 400-4000 cm-1 region with 400 cm-1 resolution [35]. The FTIR imaging is carried out using Perkin Elmer RX. The types main IR signals and functional

groups with the possible components are listed in the below tables 4.8 to 4.10. We can be observed that the treated samples are mostly like esters, alkene, aromatics, ketones and alcohol. Different types of functional groups observed, like e.g., OH (3950–3100 cm^{-1}), C=H (2900–2100 cm^{-1}), C=O (2000-1750 cm^{-1}), C=H bending (1720-1450 cm^{-1}), etc. [37]. They were showed different IR sprectre structures. The highest IR absorbance of OH and C–O was found with cellulose while hemicellulose contained higher C=O compounds. Compared with cellulose and hemicellulose, a nice difference was observed in the finger print region (1830–730 cm-1) for lignin's IR spectra

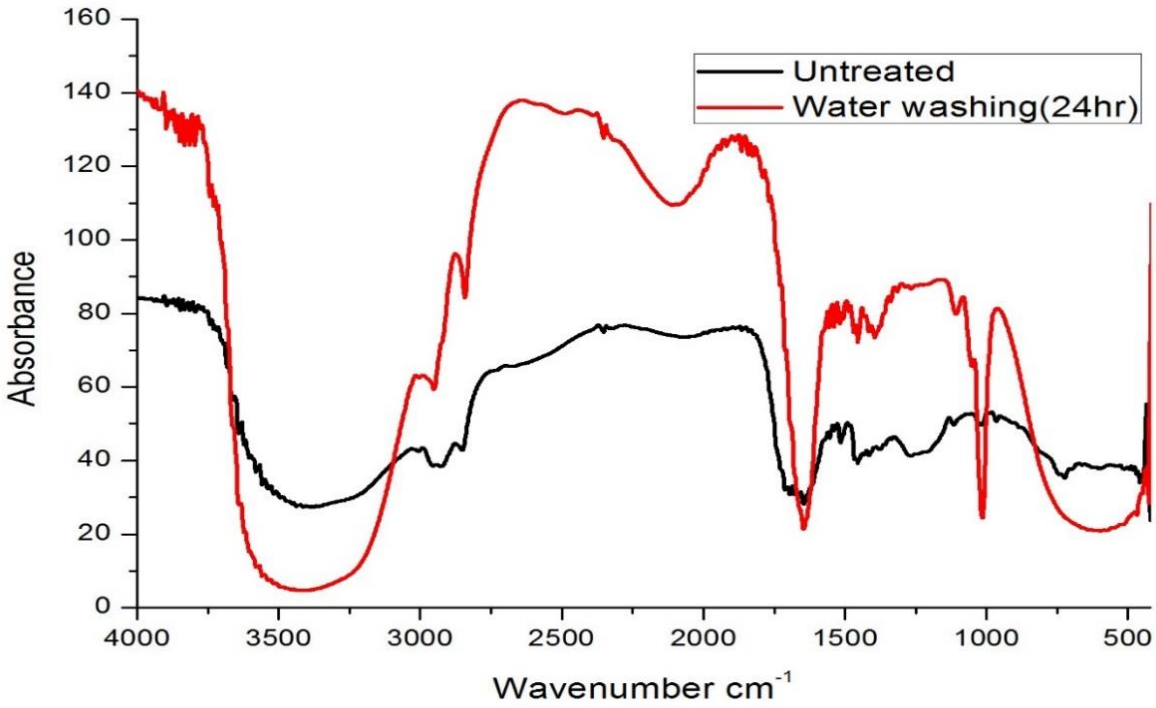

Fig 4.4 FTIR spectra of untreated and water washing (24hr) pyrolytic oil.

Table 4.8 The main functional groups in Untreated and water washing (24hr) Pyrolytic oil

Wavenumber cm^{-1}	Functional groups	Compounds
3700 – 3500	OH Streching	Alcohols and Phenols
3100 - 2900	C=C-H Streching	Aldehydes and Ketones
2260 - 2050	C=C asymmetric strech	Alkenes
1694 – 1900	C = O Bending	Esters
725 - 520	-CH Bending	Aromatic Hydrogens

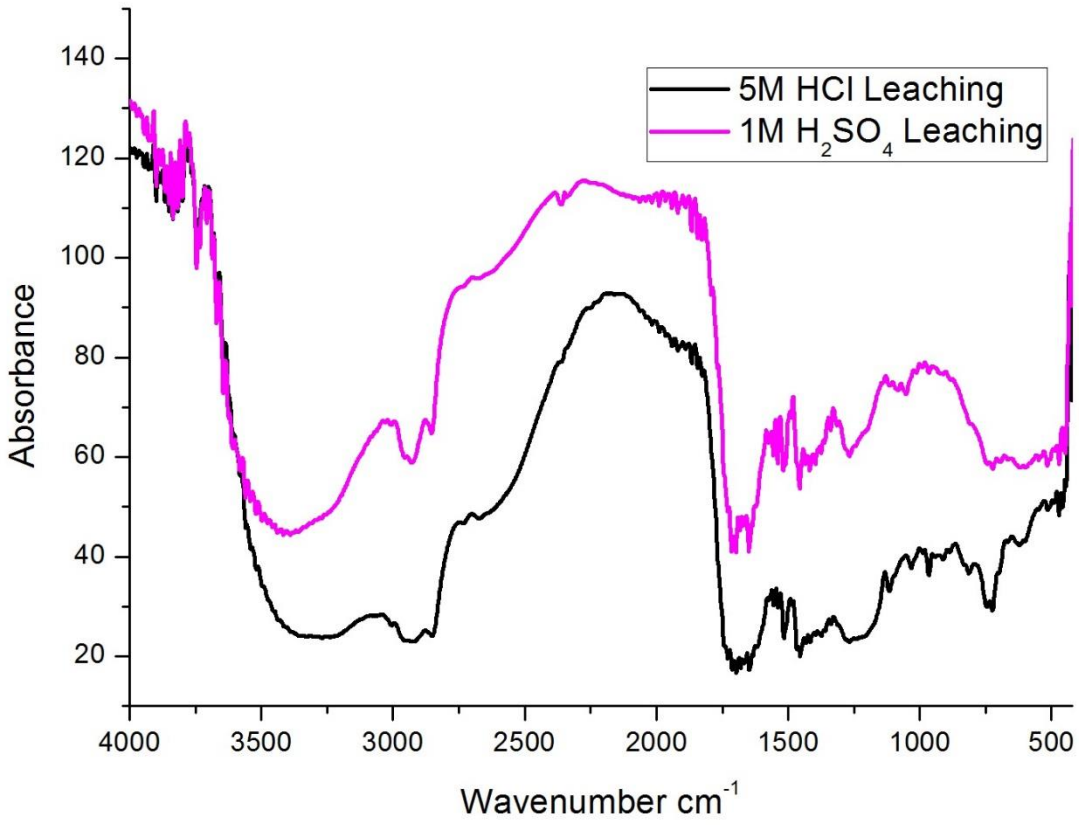

Fig 4.5 FTIR spectra of 5M HCl and 1M H_2SO_4washing pyrolytic oil.

Table 4.9 The main functional groups in 5M HCl and 1M H_2SO_4 Pyrolytic oil

Wavenumber cm^{-1}	**Functional groups**	**Compounds**
3600 - 3100	O-H Streching	Alcohols and Phenols
2900 - 2100	C-H Streching	Aldehydes and Ketones
1900 – 1750	C=O asymmetric strech	Alkenes
1700 – 1450	C=C Bending	Aromatics or alkenes
1120 - 960	C-O Strech	Ketones
725 - 525	C-H Bending	Aromatic Compounds

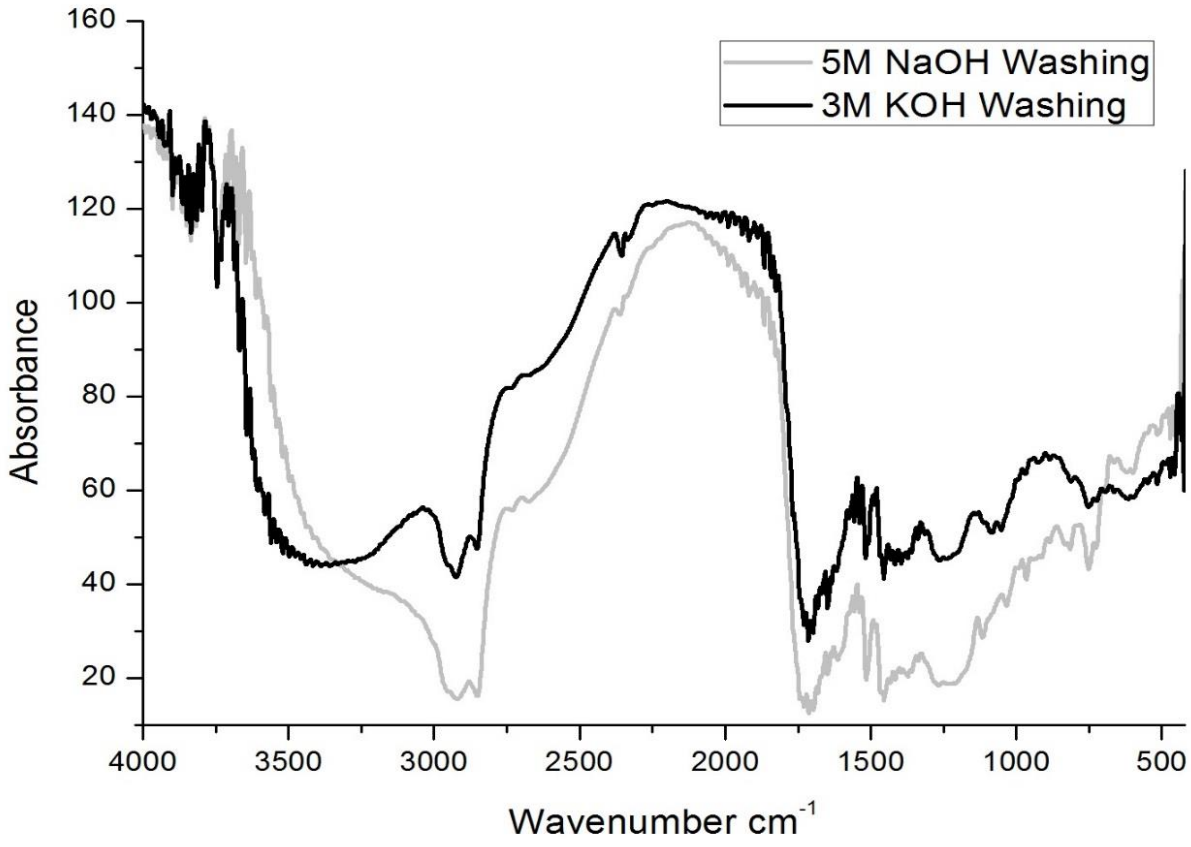

Fig 4.6 FTIR spectra of 5M NaOH and 3M KOH washing pyrolytic oil.

Table 4.10 The main functional groups in 5M NaOH and 3M KOH Pyrolytic oil

Wavenumber cm^{-1}	**Functional groups**	**Compounds**
3700 – 3100	OH Streching	Alcohols and Phenols
2900 - 2100	O-H Streching	Aromatic Hydrogens
1900 – 1650	C=O Strech	Ketones
1720 - 1515	C=C Bending	Aromatics or alkenes
1450 - 1035	C-O Strech	Esters
960 - 610	C-H Strong	Alkenes

CHAPTER – 5

CONCLUSION& FUTURE WORK

5. Conclusion

Pre-treatment of rice husk with water leaching, acid washing with dilute HCl, dilute H_2SO_4 solutions, and alkali solutions like NaOH, KOH were shown the major change in the pyrolysis product distribution. Thermal stability and rate of decomposition were observed using TG analysis of both untreated and treated rice husk material. It has shown that the present composition of rice husk biomass such as cellulose, hemicellulose, and lignin changes effectively compared to untreated biomass. The yield of bio oil increased significantly and also decreasing that the char and gas percentage of rice husk treated by acid and base solutions. Ash content is decreased through pre-treatment processes using acids and bases.

It shows the greater influence of acid and alkali treatment on the pyrolysis of rice husk dependent on the kind of acid with the order of HCl > H_2SO_4 > NaOH > KOH> water leaching. Treated rice husks have been given the higher percentage of oil compared to untreated rice husk, because it has least percentage of ions. 5M HCl leaching rice husk has been given the highest liquid product distribution at 500^oC and it is given the 57.05 wt.% total liquid .The calorific value of oil however is not affected much and is in the range of 31–34 MJ/kg. The chemicals in the bio-oil included acids, aldehydes, ketones, alcohols, phenols, sugars, *etc*. found through the FTIR. Finally, alkali solutions were not given the highest product distribution through the pre-treatment processes. Henceforth by observing all the result we can clear that the pre-treatment biomass pyrolysis oil will be a good source of energy.

Future Work:

Have to find the physical properties of treated and untreated rice husk pyrolysis oil. Surface area of the char has to also determine to find out whether it can be used as an adsorbent. Qualitative identification of volatile and semi volatile organic compounds in complex mixtures will be used through GC-MS. After finding these properties have to upgrading the both untreated and treated rice husk pyrolysis oil.

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